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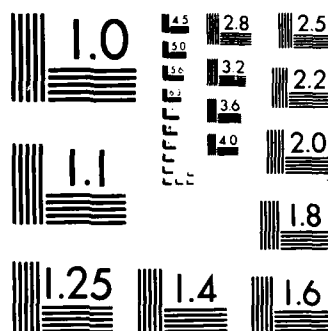UNCLASSIFIED   M G ZONNEVYLLE ET AL   JUL 87 TR-35   F/G 7/4   NL

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ELECTRONIC FACTORS IN THIOPHENE ADSORPTION AND

HYDRODESULFURIZATION ON Mo S$_2$ SURFACES

BY

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Hydrodesulfurization, the removal of sulfur in the form of H_2S from petroleum compounds, is a crucial step in industrial refinement processes. In spite of numerous recent experimental and theoretical studies, many aspects of the complex HDS system remain obscure. We will focus on the MoS_2/thiophene system in this work.

Electronic Factors in Thiophene Adsorption and Hydrodesulfurization on MoS$_2$ Surfaces

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Hydrodesulfurization, the removal of sulfur in the form of H$_2$S from petroleum compounds, is a crucial step in industrial refinement processes. In spite of numerous recent experimental and theoretical studies, many aspects of the complex HDS system remain obscure[1]. We will focus on the MoS$_2$/thiophene system in this work.

MoS$_2$ based systems are among the most frequently used and studied catalysts. The microscopic nature of the active surface is not well defined, although several points can be made. Crystalites of the material are bound to an Al$_2$O$_3$ support, which is generally considered to be inert. MoS$_2$ is a layer compound; the crystals cleave readily between the S-Mo-S sandwiches to expose all-sulfur faces. However, this surface, the basal plane, is believed to be inactive in HDS. The catalytic surface contains exposed Mo atoms. A good candidate is the edge plane perpendicular to the sulfur layers. Corner sites along the edge and defect sites arising from "missing" surface sulfur atoms, in particular, have been implicated as the active sites[2]. These Mo atoms are coordinatively unsaturated, thus it is not unreasonable that adsorption may occur here.

Thiophene (SC$_4$H$_4$) is the simplest, and most reactive, aromatic species in the HDS feedstock. Neither the geometry of adsorption nor of the active site is known. Coordination of the planar five-membered ring species directly to a surface Mo is generally assumed for both. In organometallic chemistry, both η^5–bound (coordinated to all five atoms of the ring) and η^1-sulfur bound (coordinated perpendicularly to the sulfur) species exist[3]. However, on the MoS$_2$ surface, η^2 coordination via the β-carbons, which are furthest from the sulfur, or via the S-C bond cannot be excluded. The severe experimental difficulties associated with a direct analysis of the reaction mechanism on the catalytically important surfaces have been prohibitive. However, model studies have been performed on various transition metal surfaces. On Mo(100) and Ni(100), evidence for a metallocycle formation has been found[4], whereas on Mo(110) the proposed

intermediate is an η^1-coodinated surface butyl thiolate[5].

As the organic products are mainly butanes and butenes, the S-C bonds must be severed in any case. Bonding modes which induce partial occupation of the thiophene LUMO, $3b_1$, will weaken the bond. It is a $\pi*$ orbital antibonding between S and C, and localized mainly on the α-carbon (adjacent to the sulfur). The extent of $3b_1$ occupation, as measured by the integrated projected density of states, is one criteria we can use to identify possible active sites. The orbital lies 4.4eV above the HOMO, thus sites which produce substantial occupation are also likely to be high energy sites.
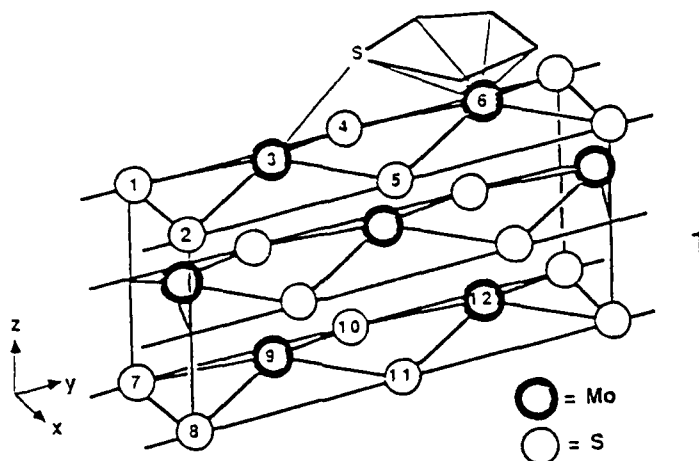
To simplify our examination of the HDS active sites, our extended Hückel calculations were performed on a three layer, one-dimensional infinite chain MoS_2 sandwich such as 1 (shown in with one particular thiophene coordination mode). The geometric specifications are taken from the real crystal strucure. Interadsorbate interactions were minimized by using a unit cell containing six atoms, four sulfur and two molybdenum, per layer. One such cell is shown; x is the direction of propegation. Atomic charges agree to within 0.005e- and overlap populations to 0.005 with those calculated for a two-dimensional MoS_2 slab (propegated in both x and y directions) with the bulk geometric parameters. The one dimensional model is appropriate for this problem as "intersandwich" interactions are negligible (at the extended Hückel level) due to the 3.17Å spacing between the sulfur layers. Similar agreement in the calculated parameters is found between one- and two-dimensional slabs with thiophene adsorbed at several test sites. The atomic parameters used can be found in reference 6.

Our model exposes two types of surface Mo atoms. Mo_3 protrudes from the surface and, with only four neighboring sulfur atoms, is coordinatively

unsaturated. Mo_9 is recessed into the face and has the full bulk compli -ment of six neighboring sulfurs. Both are electron-deficient, even with respect to the bulk (Mo: +.66, S: -.33); the net charges are +0.80 for Mo_3 and +1.13 for Mo_9. Seven geometries were considered for thiophene adsorption onto a pristine face (no defect sites). For the first set the thiophene sulfur, S_t, is bound on top of Mo_3 such that: *1)* the ring is perpendicular to the surface in the xz plane, *2)* the ring is at 45° to the surface, and *3)* the ring is parallel to the surface. The same ring orientations are selected for *4, 5* and *6* such that S_t is bridging Mo_3 and Mo_6. The sixth is an η^5 species and is shown in the schematic. The coordination of *7* is as for *1*, but to the receding Mo_9. The S_t-Mo distance is 1.90Å for all modes, which is the minimum found in Mo organometallic species[7]. Similar surface-adsorbate calculations indicate that the choice of chemisorptive bond length will alter the magnitude, rather than the direction and type, of interaction[8].

On the basis of both the S-C overlap population (o.p.) and the S-C antibonding $3b_1$ occupation, the bridging sites are substantially more effective at weakening the S-C bond than the on-top modes in any given ring orientation. Coordination to the recessed Mo has the smallest effect on this bond. The η^5 species, *6*, experiences the most severe S-C bond weakening; the o.p. drops from the molecular value of 0.887 to 0.778. The thiophene $3b_1$ occupation of 0.719e- is the largest calculated. By matching the peaks in the $3b_1$ DOS to those of the surface Mo levels, we find the primary source of backdonation to be the Mo_6 x^2-y^2 levels. The xy states are involved in the MoS_2 surface bond formation; ~40% are found in the sulfur p block. In a true C_{5v} fragment, CpM (Cp=cyclopentadienyl, C_5H_5), the xy and x^2-y^2 orbitals are degenerate and both interact with the degenerate Cp π^* orbitals[9], which become the $3b_1$ and $2a_1$ of thiophene. If sulfur atoms are sequentially removed from the surface to model defect sites, the xy levels shift out of the sulfur p block and into major peaks of the thiophene π^* states.

The $3b_1$ occupation increases for the bridging set in the order perpendicular, 45° and parallel, but much less so for the on-top set. As described earlier, the binding energies become less favorable as well. One must keep in mind, however, that our calculations produce reasonable relative energies, but unreliable absolute energies.

Chemisorptive bonds typically have two components: adsorbate to surface donation and surface to adsorbate backdonation. The two sulfur

lone pair orbitals, $2b_1$ perpendicular to the ring and $9a_1$ in the ring plane, figure prominently in the former. Thiophene is a much better donor than acceptor adsorbate, as the LUMO is not only localized at the α-carbon and very high in energy, but the sulfur lone pair orbitals are only ~2eV below the fermi level. The projected DOS's indicate that for each of the geo- metries, the more important of the two is the one best able to interact with the Mo yz states. For the on-top geometries, the interaction is π-bonding, involving $2b_1$ for the perpendicular site *1* and $9a_1$ for the parallel *3*. The lone pair oriented radially, rather than tangentially, with respect to the $Mo-S_t-Mo$ angle dominates the bridging modes ($9a_1$ for the perpendicular *4* and $2b_1$ for the parallel *6*). A comparison of the dis- persion and charge transfer out of the lone pairs shows that bridging thiophene is a superior electron donor to on-top thiophene. The direction of net charge flow is exclusively from the adsorbate to the substrate, and into the uncoordinated surface or bulk Mo atoms. Coordinated Mo atoms tend to be further oxidized. The most profound effect is the +1.27 charge at the η^5 Mo relative to the bare surface.

The sequential removal of three of the four sulfur neighboring a coordinated Mo atom brings out a problem inherent in non-infinite models, that being, what charge to assign to the non-stoichiometric unit cell. The problem will be addressed in more detail in a subsequent work. Regardless, the effect on the dispersion and distribution of the thiophene orbitals is significant in most coordination geometries. We discuss only the η^5 case here. As previously mentioned, the Mo xy becomes increasingly involved in backbonding. The important thiophene $3b_1$ and $2b_1$ become more compact as they interact with less difuse Mo orbitals (fewer MoS_2 surface bonds). Assuming a constant fermi energy to circumvent the aforementioned charge problem leads to a slight increase in the $3b_1$ occupation (~5% total) and decrease in the S-C o.p. (~10% total).

Our extended Hückel calculations implicate η^5-bound thiophene as a possible active species for HDS. Defect sites may be more reactive. Certainly more geometries must be explored before a definitive active site is discovered.

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